

THE SOURCES OF CARCINOGENIC PAH EMISSION IN ALUMINIUM PRODUCTION USING SODERBERG CELLS

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Abstract: Specific yields were determined for tars, benzo(a)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene from the main PAH sources in aluminium production using Soderberg cells with anode pastes based on medium- (MP) and high- (HP) softening-point pitches. It was evaluated that the most significant source of carcinogens from the Soderberg cell is the open hole during the process stage of repositioning the current-carrying studs. This phase of the work contributes about 60-70% of the total carcinogenic PAH emissions to the atmosphere. It is shown that a replacement of MP with HP results in a decrease of the specific tar yields from all sources, but it does not reduce the specific yield of the carcinogenic PAHs and therefore the carcinogenic danger of this technology.

Key words: aluminium production; anode pastes; carbonisation; carcinogenic PAHs; coal-tar pitches; Soderberg cell.

1. INTRODUCTION

About 2M tons of aluminium is currently generated by the plants in Siberia. Unfortunately only a minor part is generated using the currently environmentally-appropriate “prebaked” technology, which ensures low specific yields of tar that contain carcinogenic polycyclic aromatic hydrocarbons (PAHs) (0.06 kg/t Al based on data from the Pechiney Company). Instead the majority of aluminium is generated in Soderberg cells with self-baking anodes, which generates the highest carcinogenic risk

in aluminium production. The specific tar yields are considerably higher for aluminium productions that use Soderberg technology, producing 0.21 kg/t Al with a 'dry' gas cleaning system (Reynolds Company) and up to 0.65 kg/t Al with a 'wet' gas cleaning system at the Krasnoyarsk aluminium plant (Kaiser Aluminium & Chemical Corporation) (Johnson and Lobachev, 1998). The reduction of carcinogenic PAH emissions is ecologically very significant for large centres of aluminium production using Soderberg technology (Krasnoyarsk, Bratsk, Irkutsk, Novokuznetsk).

When determining specific yields of tar and carcinogenic PAHs using Soderberg technology, emissions from the gas cleaning system and gas escapes from under the gas skirt are traditionally considered while the process stage of current-carrying stud repositioning is not. It is important to evaluate the contribution of two major sources of atmospheric PAH emissions: 1) gases formed during slow (0.01-0.1°/min) carbonisation of 'dry' anode paste and anode body formation; and 2) gases released from the open hole during stud repositioning, when rapid heating (70-100°/min) pyrolysis of the studhole anode paste takes place, and 'secondary' anode formation.

The use of high-softening-point pitches (HP) instead of medium-softening-point pitches (MP) to prepare the anode paste is considered one of the ways to reduce the environmental danger. Such a replacement is associated with economic and technological advantages due to a decrease in anode paste consumption and a decrease in specific tar yields, which should in turn result in a decrease of carcinogenic PAH yields. However, it has not been proven that a switch from MP to HP will decrease the carcinogenic danger. As such it is important to compare the carcinogenic PAH yields of carbonisation products of MP, HP and anode pastes based on MP (APMP) and HP (APHP).

The objectives of this work are to evaluate the contributions of the main sources of carcinogenic PAH emissions and to compare their carcinogenic danger during aluminium production using Soderberg cells.

2. EXPERIMENTAL

Samples of medium- and high-softening-point coal-tar pitches were used under laboratory conditions. The elemental composition and technical characteristics of the pitches are presented in Table 1. Samples of industrial 'dry' anode pastes were used which contained petroleum coke calcined at 1,200°C and 30.5 wt.% MP or 27 wt.% HP. Studhole anode paste was also used, which contained 37 wt.% MP or HP (APMP and APHP).

The experimental techniques for simulating the formation of slow (1°/min) and rapid (70°/min) carbonisation were described by Koptyug et al. (1997) and Anshits et al. (2001). Extraction of industrial dust and carbon residues was described by Kurteeva et al. (2002). Analysis of PAHs in pyrolysis tars and extracts was carried out using the U.S. EPA method number 610, using a micro-capillary quartz column with an SE-54 immobilized silicone phase (12 m x 0.2 mm x 0.3 µm). The overall content of anthracene and phenanthrene (A+Ph) was determined, as well as the contents of the following individual PAHs: fluoranthene (Fl), pyrene (Py), benz(a)anthracene (BaA), chrysene (Chr), benz(b)fluoranthene (BbF), benz(e)pyrene (BeP), benz(a)pyrene (BaP), dibenz(ah)anthracene (DBA), benz(ghi)perilene (BP). The sum of the PAHs (ΣPAH) was determined as a summary content of A+P and 9 individual PAHs.

Table 1. The elemental composition and technical characteristics of the studied pitches.

Parameter	High-softening-point pitch	Medium-softening-point pitch
Softening point, °C	110-113 (Metler)	75-77 (ring-rod)
Content, wt. %:		
Insoluble matter:		
In toluene	25.6-26.4	26.0-28.0
In quinoline	6.0-7.0	10.0-13.8
Volatiles	56	55-58
Ash	0.16-0.20	0.10-0.20
Content, wt. %:		
C	92.46-93.01	91.66-92.48
H	4.00-4.40	3.90-4.10
N	1.00-1.08	1.52-1.75
S	0.27-0.36	0.16-1.27
O (determined by difference)	1.44-1.78	1.46-1.76
C/H	1.75-1.94	1.80-1.88

3. SIMULATION OF SODERBERG ANODE FORMATION UNDER LABORATORY CONDITIONS

Simulation of industrial carbonisation conditions permits an estimate of the ecological danger caused by the various process stages when using different feedstock. As such a laboratory study of MP, HP and APMP, APHP was carried out under conditions which simulate both regimes of Soderberg anode formation: slow (1°C/min) carbonisation of 'dry' anode paste and formation of the anode body, and rapid heating (70°C/min) carbonisation of the studhole anode paste and formation of a 'secondary'

anode. To take into account random feedstock variations a required number of experimental data was treated statistically.

The dynamics and content of the main products (gases, tar containing PAHs, carbon residue) during slow ($1^\circ/\text{min}$) carbonisation of MP and HP have been studied. During pitch carbonisation ($1^\circ/\text{min}$) the formation of the main (H_2 , CH_4) (Fig. 1) and minor gases (C_2H_6 , C_3H_8 , CO) were observed. Intensive gas generation was observed in the low- ($480\text{-}530^\circ\text{C}$) and high- ($640\text{-}750^\circ\text{C}$) temperature intervals, with rate peaks occurring at $460\text{-}500^\circ\text{C}$ and 720°C . The generation of ethane and propane was only observed in the low-temperature interval. Within the high-temperature interval the peak gas generation rates for MP were higher compared to those for HP. For both pitches a steady hydrogen generation rate was observed within the temperature range of $500\text{-}800^\circ\text{C}$ (Fig. 1).

The thermochemical conversion processes were accompanied by thermal effects, predominantly with heat absorption in the low-temperature range ($460\text{-}520^\circ\text{C}$) and heat release in the high-temperature range ($680\text{-}720^\circ\text{C}$) (Fig. 1). For MP there was a retarding (by $50\text{-}100^\circ\text{C}$), a cessation in growth, or even a decrease in temperature in the reaction layer of a pitch sample as compared with the furnace temperature in the low-temperature range. The temperature rise rate increased in the high-temperature range. The thermal effects here are considered minor during HP carbonisation (Fig. 1). The main tar release occurs from 640 to 750°C , at the same time as the gases, while the main release of carcinogenic PAHs (BaP, DBA, BP) occurs within $700\text{-}800^\circ\text{C}$ (Fig. 2).

Thus the study of the dynamics of the main products formed during MP and HP slow ($1^\circ/\text{min}$) carbonisation indicates two intervals of intensive gas generation: the low- and high-temperature areas, with peaks of gas generation rates at $460\text{-}500^\circ\text{C}$ and 720°C along with the simultaneous generation of tar and carcinogenic PAHs within the high-temperature interval.

During the current-carrying stud repositioning stage, anode paste is placed into the open hole. The hole bottom temperature is $700\text{-}850^\circ\text{C}$, and thus rapid pyrolysis of the anode paste takes place along a front of high temperature heating.

The laboratory study showed that the tar yields during rapid heating carbonisation of APMP and APHP are about 10 times higher (and yields of carcinogenic PAHs are about 5-30 times higher), than with slow carbonisation of both anode pastes (Fig. 3). Based on this it was shown that the most significant source of atmospheric emissions of carcinogenic PAHs is the open hole, where rapid heating carbonisation of the studhole anode paste takes place.

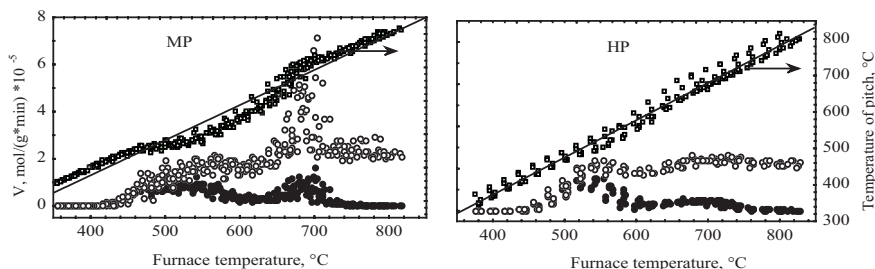


Figure 1. Variations in the formation rate of hydrogen (°), methane (●) and temperature of pitch samples (□) with furnace temperature ramping (heating rate 1°C/min) during carbonisation of MP (sampling 16) and HP (sampling 7).

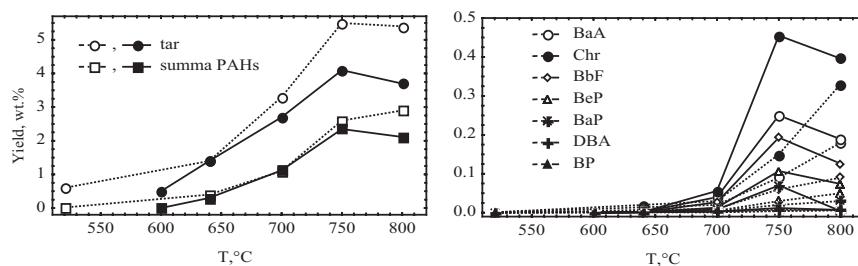


Figure 2. Dependence of tar and PAH yields on carbonisation (heating rate 1°C/min) temperature of MP (---) and HP (—).

It was established that the tar yields during slow and rapid heating carbonisation of HP and APHP are reduced approximately 1.5 times as compared with MP and APMP. These results verify data by Mirtchi et al. (1995) and Sertakov et al. (1998) regarding a decrease in tar yields when using HP instead of MP. However, the yields of BaP and other carcinogenic PAHs are not reduced (Fig. 3), and thus the replacement of MP with HP does not result in a decrease in the yield of carcinogenic PAHs and, therefore, the carcinogenic danger of Soderberg technology.

Under actual industrial conditions, tars containing carcinogenic PAHs are generated in an adsorbed state on the surface of dispersed particles such as soot, alumina (Lane, 1989). In order to understand how well the laboratory experiments represent true industrial conditions, a comparison was made of the profiles of PAHs generated from anode paste pyrolysis tars in the laboratory and the profiles of extraction tars of industrial dusts and slimes from the Krasnoyarsk aluminium plant (KrAZ), for both carbonisation regimes. Earlier these profiles were analysed by Anshits et al. (2001), and it

was shown that they are practically identical. Based on these results one can conclude that the laboratory data can be used to assess the carcinogenic danger of slow and rapid heating stages of Soderberg anode formation.

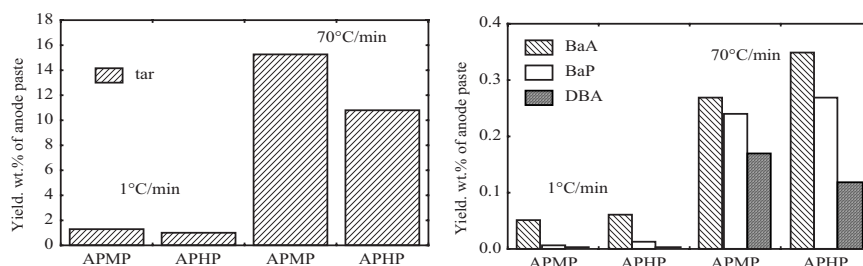


Figure 3. Yields of tars and carcinogenic PAHs of slow (1°/min) and rapid (70°/min) heating carbonisation of anode pastes based on the medium- (APMP) and high- (APHP) softening-point pitches. Sampling for the slow carbonisation : 8 for APMP, 9 for APHP; sampling for the rapid heating carbonisation : 3 for APMP, 5 for APHP.

4. EVALUATION OF INDUSTRIAL SOURCES OF PAH EMISSIONS UNDER THE CONDITIONS OF SODERBERG ANODE FORMATION

Specific yields of tar and carcinogenic PAHs generated from the main technogenic sources from KrAZ when using APMP and APHP were calculated using the Methodika VAMI (1988). This method uses anode paste consumption values, the efficiency factors for all gas cleaning system devices, the permeability of the gas skirt, and the results of laboratory research into carbonisation of pitches and anode pastes based on these pitches.

As an example, Figure 4 schematically illustrates the balance of specific yields of tar and the most dangerous carcinogenic PAHs (BaA, BaP and DBA) from the main sources of the KrAZ Soderberg electrolyser when using APMP and the 'wet' gas-cleaning system. The local sources of tars containing PAHs include:

- emission from the hole during stud repositioning;
- gas escape from under the gas skirt;
- emission of the 'wet' gas-cleaning system;
- slimes during slime storage.

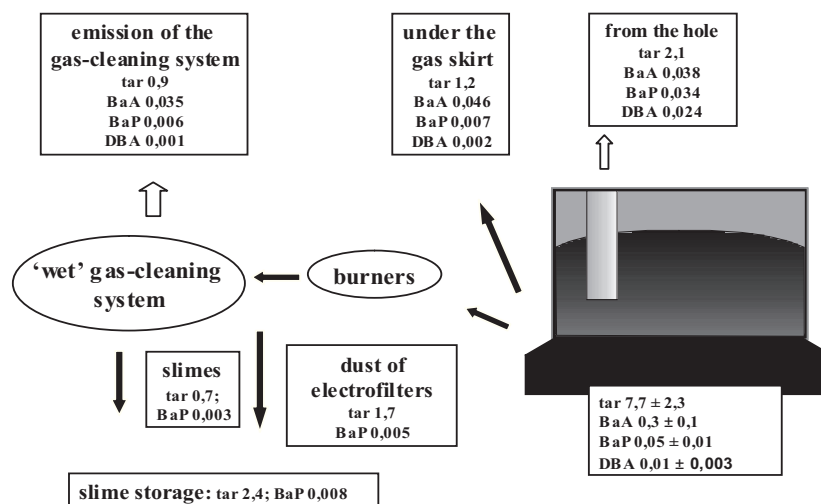


Figure 4. Specific yields of tar and carcinogenic PAHs from the main sources of the KrAZ Soderberg electrolyzer using anode paste based on medium-softening point pitch and 'wet' gas-cleaning system.

Rapid carbonisation of the studhole anode paste determines the emissions from the hole, slow carbonisation of 'dry' anode paste determines other emissions.

It is interesting to compare the specific yields of carcinogenic PAHs generated from the main local sources, i.e. from the hole during stud repositioning, gas escape from under the gas skirt and emission of the gas-cleaning system. The calculated specific yield values of tar and carcinogenic PAHs (BaA, BaP and DBA) from the main sources when using anode pastes based on MP and HP, and 'wet' and 'dry' gas-cleaning systems, are presented in Table 2.

These results indicate that the most dangerous local source of carcinogenic PAHs is emission from the open hole at the process stage of stud repositioning, which is about 60-70% of the total atmospheric emission. It stipulated low specific tar yields in aluminium production using the Soderberg technology of the Reynolds Company, Kaiser Aluminium & Chemical Corporation and other firms. In particular, when using HP-based anode paste the specific yield of BaP from the hole is 0.037 kg/t Al while the total atmospheric emission is 0.048 kg/t Al, which includes emissions from the hole, gas escape from under the gas skirt, and emissions from the 'dry' gas cleaning system. Traditionally this source has not been considered in calculations of specific yields of tar. Thus, the calculated total specific yield

of tar when using APMP is 2.1 kg/t Al, excluding emissions from the hole (Table 2), which corresponds to data reported for the Krasnoyarsk aluminium plant (2.09 kg/t Al - Zhuravlev and Petushkov, 1998). When using HP, the specific tar yield is 0.9 kg/t Al excluding emissions from the hole (Table 2). There is a good correlation with data from the KrAZ-Kaiser-VAMI project (Johnson and Lobachev, 1998) – 0.39-0.65 kg/t Al. The total emission of carcinogenic PAHs in this project is reduced due to the use of the ‘dry’ gas cleaning system, and not due to the replacement of MP with HP.

Table 2. Specific yields (kg/t Al) of tar and carcinogenic PAHs from the main sources of technogenic waste produced by the Krasnoyarsk aluminium plant when using anode pastes based on MP (APMP) and HP (APHP).

Technogenic emission	APMP				APHP			
	tar	BaA	BaP	DBA	tar	BaA	BaP	DBA
From the hole	2.1	0.038	0.034	0.024	1.5	0.049	0.037	0.017
From under the gas skirt	1.2	0.046	0.007	0.002	0.8	0.048	0.009	0.002
From the gas cleaning system:								
‘wet’	0.9	0.035	0.006	0.001	0.6	0.036	0.007	0.0016
‘dry’	-	-	-	-	0.1	0.006	0.002	0.0002

A replacement of APMP with APHP in aluminium production using Soderberg cells results in a decrease in the yield of tar from all local sources. However, in this case the yield of BaP and other carcinogenic PAHs from these sources is not reduced.

5. CONCLUSIONS

The laboratory research into slow and rapid carbonisation of MP and HP, and anode pastes based on these products, has been studied. The dynamics and the content of the main products formed (gases, tar containing PAHs, carbon residue) during slow (1°/min) carbonisation of MP and HP have been studied.

It was shown that during rapid (70°/min) carbonisation of anode pastes, the yields of tar are about 10 times higher and yields of carcinogenic PAHs are about 5-30 times higher than with slow carbonisation. Based on this, the most significant source of carcinogenic danger of Soderberg cells was found to be the open hole during the process stage of repositioning the current-carrying studs. Despite the finding that this stage contributes 60-70% of the

carcinogenic emissions of PAHs to the atmosphere, this source is traditionally not considered.

Specific yields were determined for tars, BaA, BaP and DBA from the main sources of PAHs in aluminium production using vertical stud Söderberg cells with anode pastes based on MP and HP. It was shown that use of HP in the anode pastes results in a considerable decrease of specific tar yields from all sources, as compared with MP, while the specific yields of BaP and other carcinogenic PAHs does not change significantly. A replacement of MP with HP in aluminium production using Söderberg technology does not reduce the carcinogenic danger of this production technique.

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